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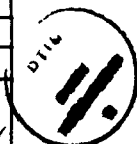
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**ENGINEER RESEARCH  
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Report 1015

SILICON MONOXIDE PROTECTED

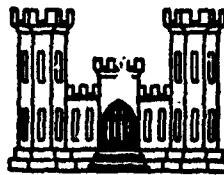
FRONT SURFACE MIRRORS

Project 8-23-02-002  
(XR 750)

13 October 1947

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Report 1015

SILICON MONOXIDE PROTECTED FRONT-SURFACE MIRRORS

Project 8-23-02-002  
(XR 750)

13 October 1947

Submitted to  
THE CHIEF OF ENGINEERS

U. S. Army  
Washington, D. C.

FOR OFFICIAL ACTION

by

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and  
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Radiation Branch  
Engineer Research and Development Laboratories  
Fort Belvoir, Virginia

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## SUMMARY

1. Subject. This report covers studies of the structure and properties of evaporated thin films of aluminum and silver, and describes a simple, high-vacuum evaporation process for producing high-reflecting front-surface mirrors with durable protective films of silicon monoxide. Aluminum is selected as the reflecting material because evaporated aluminum films not only adhere to the mirror base with greater tenacity but also have a high reflectivity in nearly all useful spectral ranges and a much finer grain and smoother surface than similar silver films. This last factor is important for the deposition of effective protective films on mirrors and for the minimization of diffuse reflection. For protective films, silicon monoxide was selected after investigation of the oxides of silicon. Silicon monoxide is evaporated onto the mirror surface from electrically heated tungsten, tantalum, or molybdenum boats. The silicon monoxide, which deposits in uniform, adherent layers, partially oxidizes to silicon dioxide when it is exposed to the atmosphere. The properties of magnesium fluoride protected mirrors are compared with those of silicon monoxide protected mirrors.

2. Conclusions. The report concludes that front-surface mirrors are necessary whenever maximum reflectivity and/or highly precise control of optical reflections is required, that silicon monoxide protected front-surface mirrors with aluminum reflecting surfaces on glass bases have good abrasion, corrosion, and thermal shock characteristics which make them particularly suitable for use in military equipment under all climatic conditions; that silicon monoxide protected front-surface mirrors with aluminum reflecting surfaces on glass bases have reflectivities in the visible and infrared not significantly lower than those of the unprotected metal but absorb in the ultraviolet; that silicon monoxide protected front-surface mirrors are much superior in corrosion resistance to magnesium fluoride protected front-surface mirrors, and that evaporated aluminum films are more suitable for the reflecting surfaces of front-surface mirrors than silver films.

3. Recommendations. The report recommends that silicon monoxide protected front-surface mirrors with aluminum reflecting surfaces be used in military equipment which requires maximum reflectivity and/or precise control of visible or infrared radiation by mirrors subject to exposure to natural conditions.



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FINAL REPORT

SILICON MONOXIDE PROTECTED FRONT-SURFACE MIRRORS

I. INTRODUCTION

1. Subject. This report covers studies of the structure and properties of evaporated thin films of aluminum and silver, and describes a simple, high-vacuum evaporation process for producing high-reflecting front-surface mirrors with durable protective films of silicon monoxide.

2. Authority. The authority for this work is contained in a letter from the Chief of Engineers to the Engineer Board, dated 14 October 1946, file 400.1 (XR 750), subject: Infrared Optical Materials, Approval of Military Characteristics and Authorization of Development Project XR 750. A copy of this letter is contained in Appendix A.

3. History. During World War II, a process for producing front-surface mirrors, protected with a thin film of silicon monoxide, was developed in Germany by Dr. Georg Hass of the Danzig Institute of Technology. Work on this process, classified as "Secret" by the German Government, was begun in the United States by Mr. Noel Scott of the Engineer Research and Development Laboratories in October 1945. Mr. Scott's initial efforts were based on information contained in the Joint Intelligence Objectives Agency's Report No. 9, "German Vacuum Evaporation Methods of Producing First Surface Mirrors, Semi-transparent Mirrors, and Non-reflecting Films," dated 22 September 1945, by Captain John R. Whipple, who had been detailed from the Engineer Research and Development Laboratories to the Combined Intelligence Objectives Sub-committee, Intelligence Division, Office, Chief of Engineers, TSFET (Rear), for an investigation of German infrared and searchlight developments. Shortly thereafter, Mr. Scott obtained additional information from Technical Report No. 473-45 of the U. S. Naval Technical Mission in Europe, titled "Some German Developments on Inorganic Films of Optical Thickness," dated September 1945. On 1 May 1946, Dr. Georg Hass arrived at the Engineer Research and Development Laboratories. In the following year, Mr. Scott and Dr. Hass succeeded in reproducing and improving the German evaporation apparatus using American equipment, and in improving the process for producing silicon monoxide protected front-surface mirrors.

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## II. INVESTIGATION

### A. Structure and Properties of Evaporated Aluminum and Silver Films

4. General. The most frequently used mirror metals are silver and aluminum because they have higher reflectivity in the visible spectrum than other metals. In order to select the optimum metal for front-surfaced mirrors as well as the most suitable evaporation conditions, Dr. Hass in Germany studied the structure and properties of silver and aluminum films produced in various thicknesses under various high-vacuum evaporation conditions. Dr. Hass' studies were checked in part at the Engineer Research and Development Laboratories. The results of the studies are set forth in subsequent paragraphs of this section.

5. Electron Microscope Studies. The following electron micrographs of silver and aluminum films have the same magnification. Fig. 1 presents a comparison of silver and aluminum films condensed in different thicknesses under good vacuum conditions (less than  $10^{-4}$  mm Hg) on bases at room temperature. For both metals, the grainedness, and therefore the roughness, of the film surface increase with film thickness. For equal film thicknesses, the silver surfaces are much rougher than those of aluminum. Fig. 2 shows three thicknesses of silver films condensed on bases at a temperature of 300 C. A comparison of the silver films of Fig. 1 with those of Fig. 2 indicates that elevating the temperature of the base causes much rougher and more granular silver films. A similar result is shown for aluminum films in Fig. 3. In practice, the heating of the mirror form must be avoided when depositing silver as a reflector material, and the temperature of the mirror form when depositing aluminum should not be greater than 150 to 200 C to avoid harmful roughness.

6. Optical Constants. The optical constants of silver and aluminum films for various wavelengths of the visible spectrum were calculated from data obtained by measurements in accordance with the polarization methods of Drude.<sup>1</sup> The measurements were made in high vacuum immediately after condensation of the films. The exact arrangements for these measurements are described by Dr. Hass.<sup>2</sup> Table I sets forth the optical constants thus determined, together with measured reflectivities.

7. Evaluation. Since the extinction coefficient of silver is much smaller than that of aluminum, thicker films of silver than of aluminum are required for opacity. Aluminum requires a film

1. P. Drude, Wied Ann Phys 39, 481 (1890).

2. G. Hass, Ann Phys Lpz 31, 245 (1938); and Optik 1, 8 (1946).

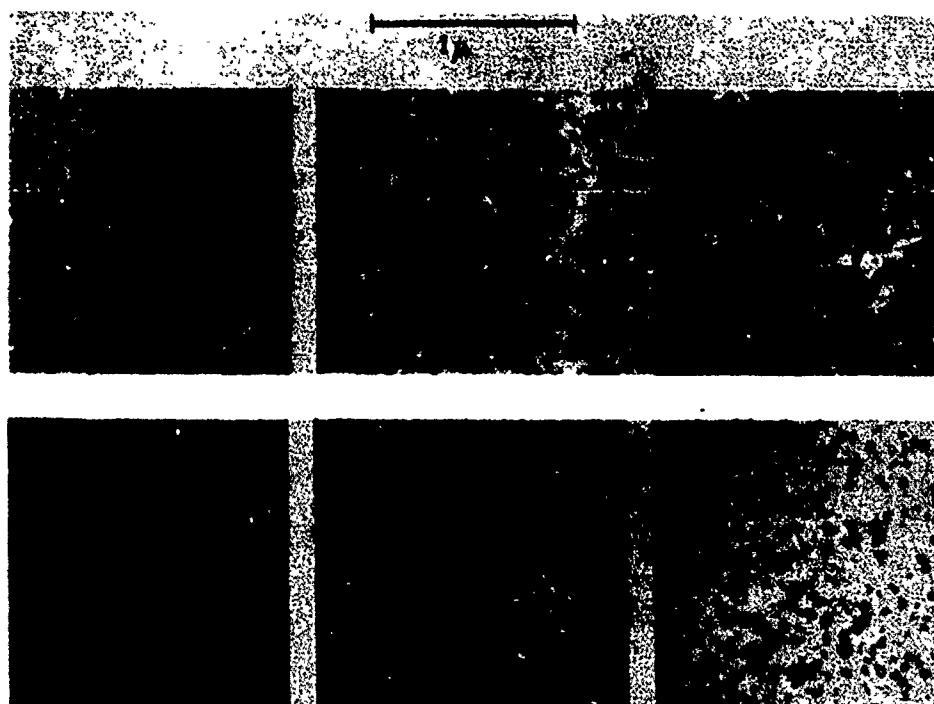


Fig. 1. Electron micrographs of films condensed to various thicknesses at room temperature. Top, left to right: silver, approximately 100 Å, 300 Å, and 550 Å thick; bottom, left to right: aluminum, approximately 70 Å, 250 Å, and 500 Å thick.

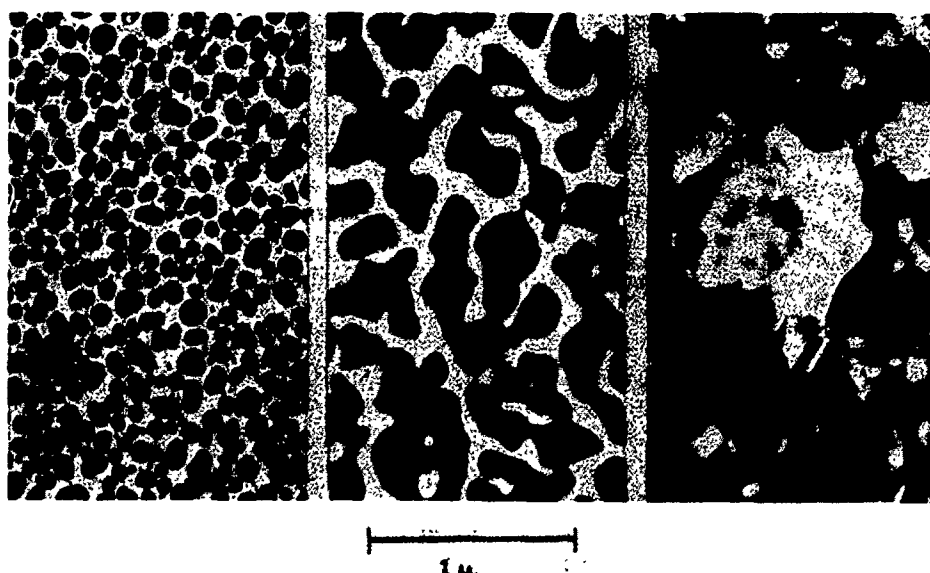


Fig. 2. Electron micrographs of silver films condensed at a temperature of 300 C to thicknesses (reading from left to right) of approximately 150 Å, 300 Å, and 600 Å.

TABLE I. OPTICAL CONSTANTS OF THE BEST SILVER  
AND ALUMINUM FILMS TOGETHER WITH MEASURED REFLECTIVITY

The constants were calculated from measurements made  
(in accordance with the polarization methods of Drude)  
in high vacuum immediately after condensation of the films

Wave- length of Light Milli- microns	Refrac- tive Index n	Coeffi- cient of Absorption k	Extinction Coefficient nk	Percent Reflectivity Calculated Rc	Percent Reflectivity Measured Rm
SILVER					
435	0.149	14.5	2.16	90.0	92.0
491	0.123	22.1	2.72	94.3	94.5
546	0.108	30.1	3.25	96.5	96.5
578	0.106	33.9	3.59	97.0	97.5
644					
ALUMINUM					
435	0.40	10.40	4.16	91.6	91.5
491	0.57	9.11	5.20	92.3	91.5
546	0.76	7.22	5.47	90.8	91.0
578	0.89	6.38	5.68	90.0	90.0
644	1.12	5.59	6.26	89.6	89.5

thickness of 500 to 600 Å to be opaque, while silver films must be thicker than 1000 Å. It follows, therefore, that aluminum-reflecting surfaces may be produced having a smoothness approximating that of the aluminum film of 500-Å thickness shown in Fig. 1, while silver reflecting surfaces will be rougher than the silver film of 550-Å thickness shown in the same figure. The greater smoothness of evaporated aluminum surfaces, the resulting minimization of diffuse reflection, and the well-known fact that evaporated aluminum films adhere to glass with greater tenacity than silver films, make aluminum a more desirable reflecting material for front-surface mirrors than silver, in spite of the higher reflectivity of the latter.

#### B. Investigation of Protective Materials

8. General. Aluminum does not tarnish as easily as silver because thin, protective films of aluminum oxide (thickness about 50 to

100Å)<sup>1</sup> are formed on aluminum when it is exposed to air. In spite of these natural films, evaporated aluminum coatings are mechanically and chemically too delicate for many mirror applications. Therefore, it is necessary to coat front-surface aluminum mirrors with a transparent, durable material.

9. Silicon Dioxide Coatings. Because of its excellent physical properties, the use of silicon dioxide was considered for protective films. Silicon dioxide can be evaporated directly onto a reflector surface; but the evaporation is difficult and the resulting films have doubtful protective qualities because of loose structure and inadequate adhesion to the mirror material.

To obtain hard, adherent films of silicon dioxide, another method was investigated. Silicon was evaporated onto the aluminum surface and oxidized to silicon dioxide by anodizing. The evaporation of silicon, which usually presents difficulties, was successfully carried out from thick (approximately 0.8 mm) tungsten boats heated electrically by a current of approximately 400 amperes. For anodizing, an ammonium tartrate bath with 3-percent tartaric acid, at a pH of approximately 5, was used. The thickness of the protective film can be determined by observing the interference colors produced by the evaporated silicon and controlled by the voltage used for anodizing. This process produces hard, adherent amorphous silicon dioxide films with good mechanical and chemical properties. However, this process requires an additional operation after the evaporation cycle, and can only be carried out with aluminum as the mirror material, because the reflecting material must be capable of forming a non-porous oxide film by the anodizing process. Aluminum is the only mirror material having this property.

10. Silicon Monoxide Coatings. To determine the suitability of silicon monoxide for protective films, thin evaporated silicon monoxide films were condensed on rock salt, released in water, and their structure studied by electron diffraction. Fig. 4, an electron diffraction pattern of an evaporated silicon monoxide film approximately 600 Å in thickness, shows only one diffuse ring with  $d$ , the periodic distance between atoms, as calculated by means of Bragg's equation ( $2d \sin \theta = n\lambda$ ), to be approximately 3.65 Å, which lies between the first pattern of silicon ( $d$  approximately 3.15 Å) and that of silicon dioxide ( $d$  approximately 4.2 Å). Therefore, this material has neither the structure of silicon dioxide nor that of silicon, and it is a homogeneous amorphous material, silicon monoxide. Its index of refraction varies with evaporation conditions and is 1.5 to 1.6 for good protective films. Silicon monoxide deposits on mirror surfaces in adherent layers. Thin films of silicon monoxide exposed to air partially oxidize to silicon

<sup>1</sup> G. Hass, Optik 1, 134 (1946).

dioxide. This oxidation stops after a very thin layer of silicon dioxide is formed on the silicon monoxide. A film of silicon monoxide 1500 Å thick is not completely oxidized after 100 hours in air at 400 C. A more thorough oxidation takes place in steam at higher temperatures.

The use of silicon monoxide as a protective film eliminates the difficulties encountered with direct evaporation of silicon dioxide, the poor qualities of the films produced thereby, and the anodizing operation required by the silicon evaporation and anodizing process..

### C. Technique for Producing Silicon Monoxide Protected Front-surface Mirrors

11. Evaporation Apparatus. The evaporator designed and assembled at the Engineer Research and Development Laboratories for the experimental production of front-surface mirrors protected by silicon monoxide is illustrated in Fig. 5. The vacuum chamber is a glass bell jar, approximately 17 inches in diameter and 27 inches high, placed on a metal base plate. Three evaporation heating elements are mounted near the base plate; two are tungsten filaments for aluminum evaporation, and the other is a tungsten, tantalum, or molybdenum boat for silicon monoxide evaporation. Current is supplied to the heating elements by four conductors, each with a capacity of 400 amperes. These conductors are insulated from the base plate with rubber gaskets. Copper rods are used as conductors within the vacuum chamber. The common conductor supports a copper bar which is connected to, and supports one end of, each heating element by means of flexible copper strips. The other end of each heating element is similarly connected to and supported by the applicable copper rod. A shield is placed between each filament and the boat to prevent mutual contamination of the materials to be evaporated.

For cleaning the mirror form by gaseous discharge, an aluminum electrode in the form of an 11-inch diameter ring, with cross-sectional dimensions of approximately 0.75 inch by 0.20 inch, is supported horizontally approximately midway between the evaporation sources and the mirror form. The perforated steel tube which supports the ring is connected to a high-voltage, direct current unit for producing a gaseous discharge at 4000 volts, 50 milliamperes. This high potential electrode is made negative with respect to the base plate which is grounded. The vacuum chamber is evacuated with a 500-liter per second oil diffusion pump backed with a 5-liter per second mechanical pump.

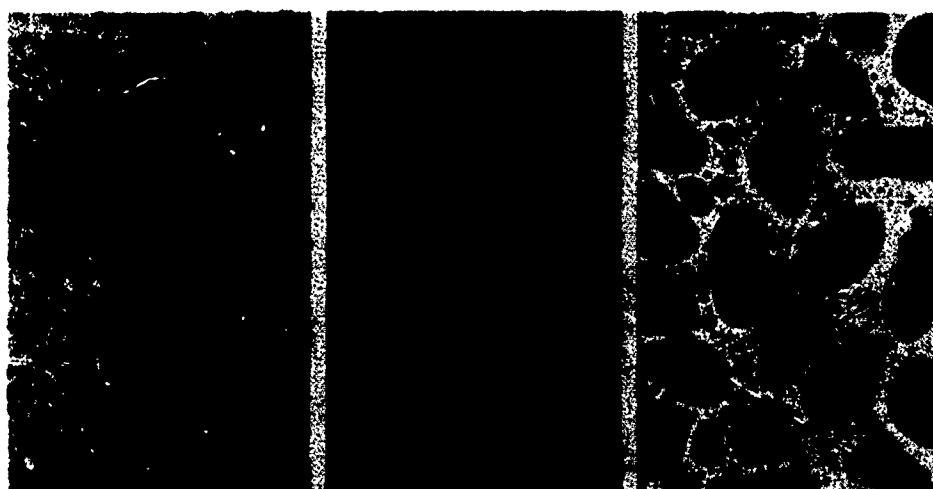


Fig. 3. Electron micrographs of aluminum films, approximately 500 Å thick, condensed at temperatures (reading from left to right) of 20 C, 150 C, and 450 C.

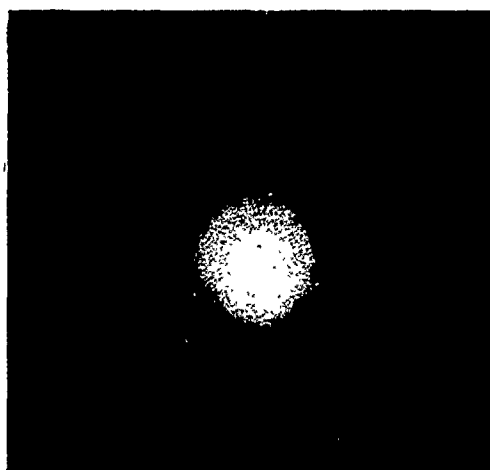


Fig. 4. Electron diffraction pattern of SiO film, approximately 600 Å thick.

Since much heat is evolved during this discharge cleaning process, the glass bell jar is protected by installing immediately inside the evaporator, a cylindrical shield of stainless steel, closed at the top. This shield also protects the inside of the bell jar from condensing metal and silicon monoxide during the evaporation process. A hole in the top of this shield permits observation of the mirror form. Two side windows, which can be opened and closed from the outside by a magnet, permit optical determination of the protective film thickness by observing the interference colors on the mirror at grazing incidence.

12. Production Technique. Silicon monoxide protected front-surface mirrors may be produced on glass, metal, or plastic bases. The techniques for their production are as follows:

a. Mirrors on Glass Bases. The glass mirror form, which has previously been cleaned with Aerosol and chromic acid cleaning solution, is placed in the usual position, approximately 20 inches above the evaporation sources. The chamber is evacuated to a pressure of about  $2 \times 10^{-3}$  mm Hg, and the high-voltage gaseous discharge is applied for 10 minutes. After the cleaning operation, the chamber is further evacuated to approximately  $5 \times 10^{-5}$  mm Hg, the current is applied to the tungsten filament, and an aluminum coating is evaporated onto the mirror form to the point of opaqueness. The aluminum evaporation must be carried out rapidly (in less than 30 seconds), because the density and optical properties of thin aluminum films depend on the evaporation speed.<sup>1</sup> Only rapidly condensed films have the density of the solid material.

The vacuum is then increased and the current is applied to the SiO-loaded boat. In practice this boat is formed in the shape of an ellipse  $2\frac{1}{2}$  inches by 1 inch from a piece of sheet tantalum 4 inches by  $1\frac{1}{4}$  inches by 0.008 inch. The current required is 250 to 300 amperes. The thickness of the SiO film produced on the aluminum surface is determined by observing the interference colors at grazing incidence. To obtain highest reflectivity in the visible, the SiO evaporation must be stopped when the interference color, after passing through the range of spectral colors, becomes a deep yellow the second time. The thickness of the SiO film is then approximately 1500 Å. This thickness of film causes the mirror to have greatest reflectivity for light in the region of 5550 Å, the region of greatest luminous efficiency. The two solid curves of Fig. 6 illustrate the decrease in visible reflection with decrease in film thickness.

1. W. Walkenhorst, Z techn Phys 22, 14 (1941); Dissertation Hannover (1946); and G. Hass, Optik, 1, 8 (1946).



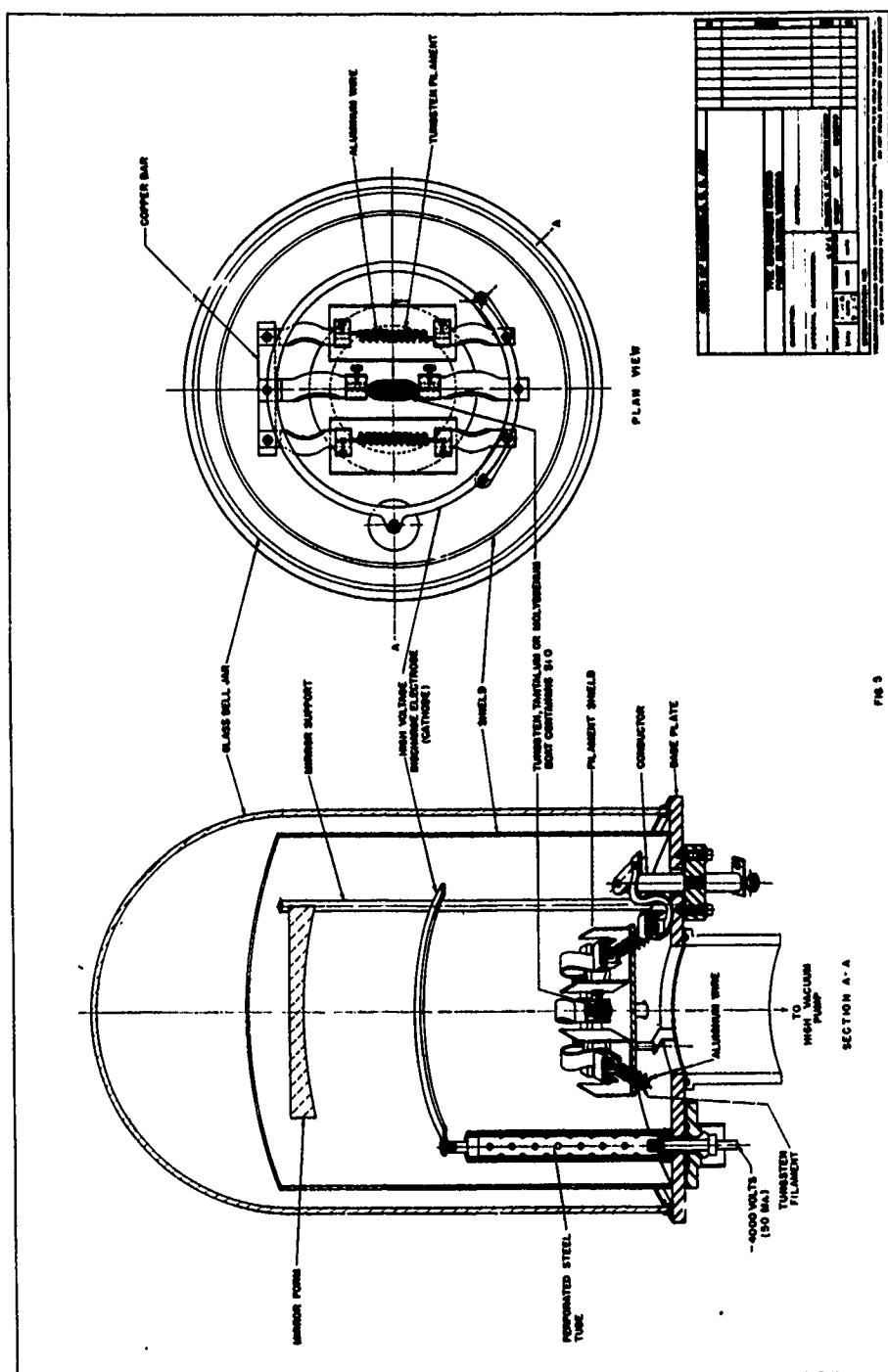


Fig. 5. Evaporator for experimental production of front-surface mirrors protected by silicon monoxide.

The evaporation of the silicon monoxide must be carried out slowly. With the Engineer Research and Development Laboratories' evaporator described in paragraph 11, eight to twelve minutes were required to produce optimum SiO films. More rapid evaporation produces yellow films composed of SiO + Si, resulting in undesirable absorption in the blue-violet region. This is illustrated by the broken line curve of Fig. 6.

b. Mirrors on Metal Bases. To coat metal, a cleaning gaseous discharge is used, employing the metal mirror form as the cathode. Then a SiO film about 2000 Å thick is evaporated onto the metal form, then aluminum, and finally, the protective SiO film. The first SiO film improves adherence of the films to the metal form, and prevents the metal of the mirror form from diffusing into the thin aluminum reflecting surface.

c. Mirrors on Plastic Bases. The plastic mirror form is subjected to a gaseous discharge for approximately 3 minutes. After one-half hour, a thin film of SiO, as determined by the first red interference color, is deposited; the reflecting surface is then made; and finally, the protective SiO film is added. As with metals, the first SiO film improves the adherence of the films.

#### D. Properties of Silicon Monoxide Protected Aluminum Front-surface Mirrors on Glass Bases

13. Reflectivity. The reflectivity in the wavelength region from 0.24 to 10 microns of aluminum mirrors, protected with a slowly evaporated silicon monoxide film of 1600-Å thickness, is shown in Figs. 7 and 8. Reflectivity of an unprotected aluminum surface is given by the top curve of Fig. 9 for the region from 0.24 to one micron. Fig. 7 shows that maximum reflectivity in the visible takes place at approximately 0.55 micron. A comparison of the curves of Fig. 7 with the top curve of Fig. 9 reveals that the reflectivity of the protected mirror for the visible is about the same as that for the unprotected mirror. On the other hand, the protected mirror shows high absorption in the ultraviolet and some absorption in the near infrared to approximately 0.95 micron. The absorption in the ultraviolet increases with speed of evaporation of the protective film (see Fig. 6). Fig. 8 shows very high reflectivity in the infrared from approximately 1 micron to 8 microns, with peak reflectivity of about 96 percent. The absorption band, characteristic of silicon oxides, appears between 8 and 9 microns.

14. Resistance to Heat and Cycles of Heat and Cold. SiO-protected aluminum mirrors on glass bases are not adversely affected by prolonged heating in air at temperatures up to 400 C, whereas the reflectivity of unprotected aluminum mirrors is substantially reduced

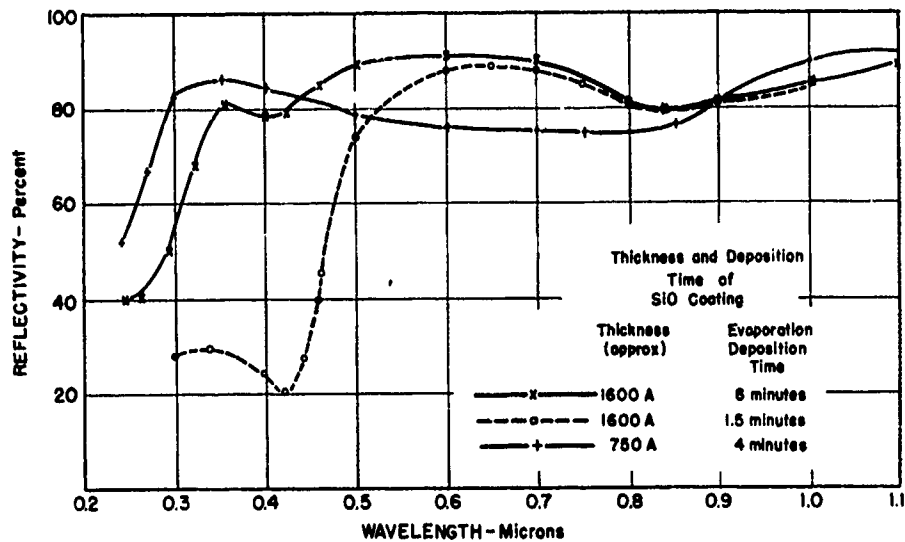


Fig. 6. Reflectivity of SiO-protected aluminum mirrors as a function of wavelength, and variation in reflectivity with film thickness and speed of evaporation. A SiO film thickness of approximately 1600 Å results in maximum reflectivity in the visible and a thickness of approximately 750 Å results in minimum reflectivity. Fast evaporation reduces reflectivity in the ultraviolet and the shorter wavelength portion of the visible.

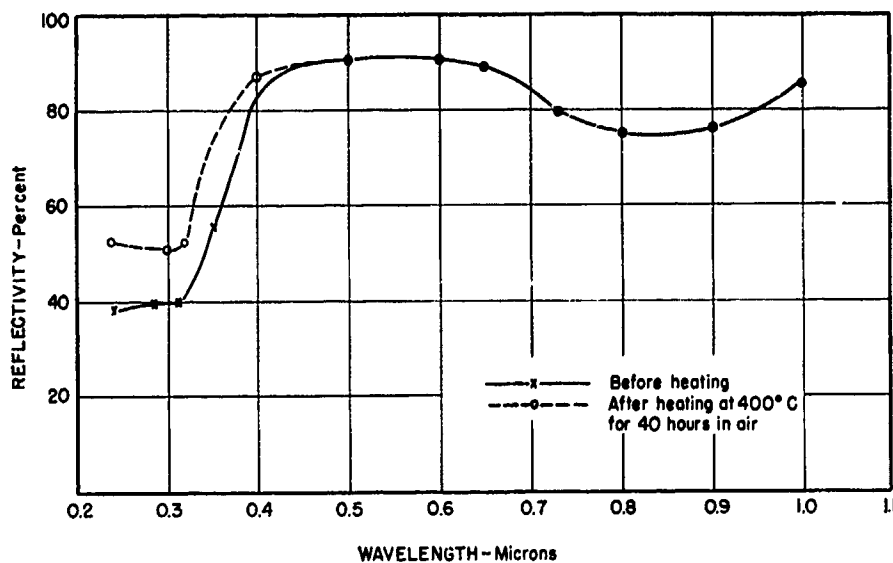


Fig. 7. Reflectivity of SiO-protected aluminum mirror before and after heating in air. Heating in air increases the reflectivity of SiO-protected aluminum mirrors in the ultraviolet without change in the visible.

by the same treatment. This is illustrated by the comparison of Figs. 7 and 9. Fig. 7 also shows that heating in air increases the reflectivity of the protected mirror in the ultraviolet. This results from oxidation of some of the  $\text{SiO}$  to  $\text{SiO}_2$ , which has higher transmission in the ultraviolet.

A very severe test to which silicon monoxide protected aluminum mirrors were subjected by a German laboratory was as follows: A mirror was taken from room temperature and placed in a steam room at 100 C. Water condensed on the cooler surface of the mirror, and the mirror remained in the steam bath until it reached the temperature of the room. The mirror was then transferred to a room at -70 C. Ice quickly formed on the mirror. Next, the mirror was transferred to room temperature until the ice melted and the mirror surface became dry. The above cycle was repeated thirty to fifty times without any damage to the silicon monoxide protected mirrors tested.<sup>1</sup>

15. Corrosion Resistance. The reflectivity of  $\text{SiO}$ -protected mirrors on glass bases is not changed by boiling in a 6-percent salt solution for periods in excess of 1 hour. These mirrors are also highly resistant to sea water, sodium hydroxide, and most acids. The protective films may be removed, however, by a hydrochloric acid-copper sulphate solution.

16. Abrasion Resistance. To simulate the most severe cleaning conditions likely to be encountered in service, the abrasion resistance of the mirrors was tested by means of a 3/4-inch steel ball covered with rough linen, loaded with a 500-gram weight, and subjected to a reciprocating motion. This test was carried out on protected mirrors before and after the heat and corrosion tests described in paragraphs 14 and 15. A protected mirror withstands more than 1000 cycles without damage, whereas the reflecting surface of an unprotected aluminum mirror is destroyed in a few cycles.

### III. DISCUSSION

17. Uses of Front-surface Mirrors. Mirrors employed in optical devices used in modern warfare must have high efficiency and be very durable to withstand various natural conditions found in all parts of the world. Among the military optical devices using mirrors are searchlights and other light projectors, infrared receivers and projectors, telescopes, periscopes, range finders, gun sights, aerial survey cameras, photogrammetric and map reading equipment, and optical testing devices. For the above applications, in which

1. Test Results of Mirrors Given to the Laboratories of Heraeus, G m b H, dated 21 October 1942, by Dr. M. Auwarter.

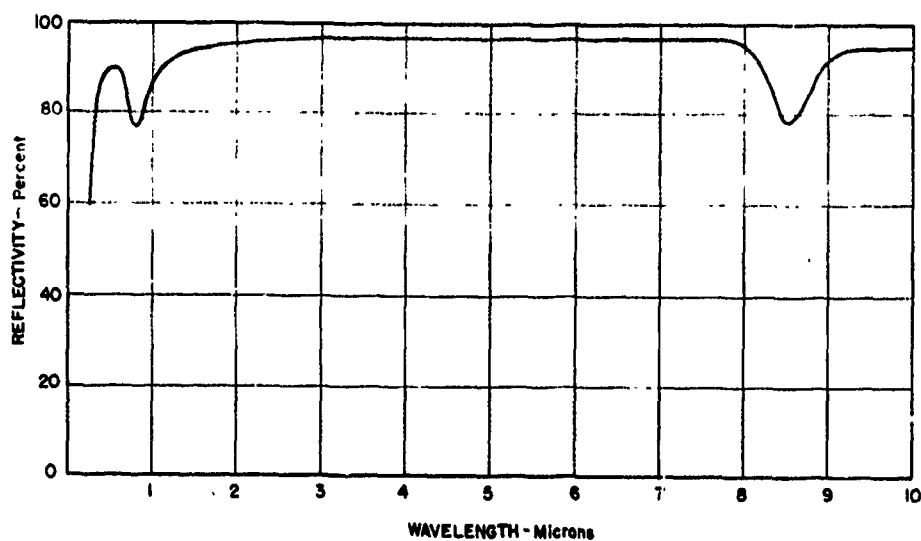


Fig. 8. Reflectivity in the infrared of aluminum mirrors with SiO protective film, approximately 1600 Å thick.

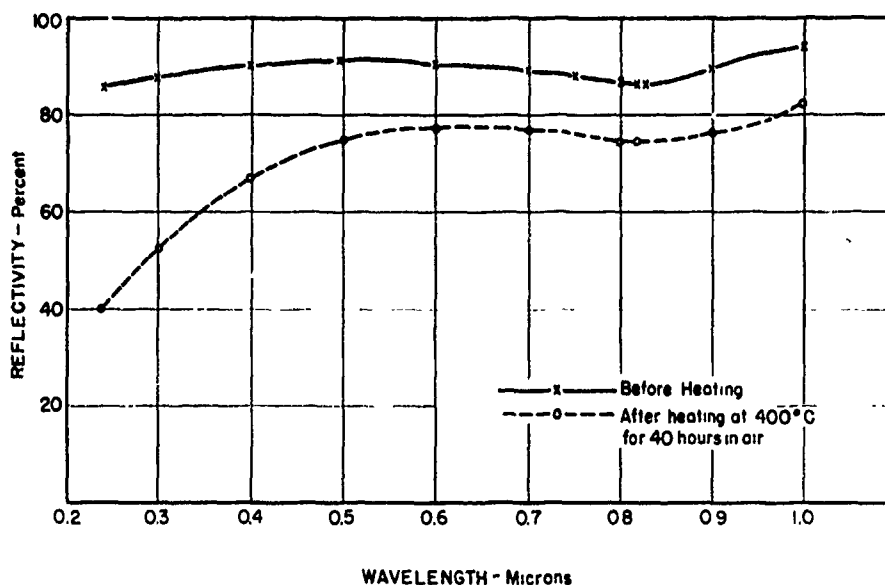


Fig. 9. Reflectivity of unprotected aluminum mirror before and after heating in air. Heating in air substantially reduces the reflectivity of unprotected aluminum mirrors because of oxidation.

maximum reflectivity and/or highly precise control of optical reflections are required, front-surface mirrors must be used. The principal deficiencies of back-surface mirrors for these applications are multiple images resulting from surface and internal reflections, and light loss resulting from absorption by the glass. Also, back-surface mirrors cannot be used in the infrared beyond 3 or 4 microns or in the ultraviolet, for glass is opaque in those regions.

18. Silver versus Aluminum for Reflecting Surfaces. The overall reflectivity of silver in the visible region is 96 percent as compared to 90 percent for aluminum. In the far infrared region, aluminum and silver have approximately equal reflectivities. In the ultraviolet region, aluminum has a much greater reflectivity than silver. Although silver has higher reflectivity in the visible region than aluminum, the latter is the better reflector material. Evaporated aluminum is much finer grained than evaporated silver for equal thicknesses of films. Also, for opacity, the thickness of silver films must be approximately double the thickness required of aluminum films. Since grainedness increases with film thickness, the roughness of the silver film increases with the thickness of the deposit. Therefore, evaporated aluminum reflecting surfaces permit finer control of optical reflections and minimize losses by diffuse reflection. Other advantages of evaporated aluminum over evaporated silver are the better adherence of aluminum to glass and the better adherence of protective films to the smoother aluminum surfaces.

19. Properties of Silicon Monoxide Protected Front-surface Mirrors on Glass Bases. The overall visual reflectivity of front-surface aluminum mirrors with a protective film of silicon monoxide approximately 1600 Å in thickness is 89 percent. This is only 1 percent below the reflectivity of unprotected aluminum (90 percent) and is 17 percent greater than the reflectivity of rhodium (72 percent), the metal least susceptible to corrosion. These same silicon monoxide protected front-surface aluminum mirrors have very high reflectivity (about 96 percent) in the infrared out to 10 microns, the limit for which measurements were made, except between 0.8 and 0.9 microns (where the reflectivity drops to 75 to 80 percent) and between 8 and 9 microns (where reflectivity averages approximately 86 percent). The absorption between 0.8 and 0.9 microns is characteristic of aluminum, and the absorption between 8 and 9 microns is characteristic of the oxides of silicon. In the ultraviolet, silicon monoxide protected front-surface mirrors are inefficient and show very high absorption in the far ultraviolet. This absorption results from the presence of silicon in the protective film; and it can be minimized somewhat by slow evaporation of the protective film, by lesser thickness of film at a sacrifice of durability, and by oxidizing more of the silicon monoxide to silicon dioxide.

The ability of silicon monoxide protected front-surface mirrors on glass bases to withstand the most severe climatic and natural conditions is well demonstrated by the results of the tests to which the mirrors were subjected. They are not adversely affected by heating in air at temperatures up to 400 C, by exposure to temperatures as low as -70 C, by temperature shocks from -70 C to 100 C, by formation of ice, and by boiling for 1 hour in 6-percent salt solution. They show good resistance to sea water, sodium hydroxide, and most acids. The protective film is extremely hard and is "wipe-proof." Exact data on the temperature, corrosion, and abrasion properties of silicon monoxide protected front-surface mirrors on metal and plastic bases are not available at this time. However, it is obvious that such mirrors will be vastly improved by the protective film, and that their limitations will result chiefly from the limitations of the metal or plastic base.

The above qualities make silicon monoxide protected front-surface mirrors particularly desirable for use in military equipment utilizing mirrors for the reflection of visible or infrared radiation. They should not be used, however, in equipment utilizing mirrors for the reflection of ultraviolet. Also, protected mirrors are not required in hermetically sealed optical systems.

20. Comparison with Magnesium Fluoride Protected Front-surface Mirrors. Thin films of evaporated magnesium fluoride have been used extensively as low-reflectance coatings for lenses. These films were too soft for protective coatings until 1941, when Dr. D. A. Lyon of the Naval Gun Factory discovered that they could be hardened by heating the glass in vacuum to approximately 450 F during evaporation of the magnesium fluoride. Since that time, hardened films of magnesium fluoride have been used not only for low-reflectance coatings but for protective coverings on mirrors that need to be wipe-proof. The following subparagraphs compare magnesium fluoride protected front-surface aluminum mirrors and silicon monoxide protected front-surface aluminum mirrors:

a. Manufacture. The manufacture of mirrors having magnesium fluoride protective films and the manufacture of those having silicon monoxide protective films differ in only two respects: the speed of applying the respective films, and the necessity for a heat treatment to harden the magnesium fluoride films.

(1) Magnesium fluoride films of proper thickness are condensed in 2 to 3 minutes on bases preheated to 450 F from a fused silica crucible containing thoroughly outgassed magnesium fluoride. Heat to raise the temperature of the base is obtained from an electrically heated spiral of nichrome wire wound on a form and placed above the mirror. Heat to produce evaporation is obtained from an electrically heated spiral

of 3½ turns of 20-mil tungsten wire placed immediately above, but not touching, the magnesium fluoride. The current required (approximately 25 amperes) is approximately one-tenth of that required for evaporation of silicon monoxide.

(2) Silicon monoxide films of proper thickness are condensed on the base in eight to twelve minutes from an electrically heated tungsten, tantalum, or molybdenum boat.

Although the evaporation of magnesium fluoride is accomplished much faster than the evaporation of silicon monoxide, the total times for producing magnesium fluoride protected mirrors and silicon monoxide protected mirrors are approximately equal, because of the preheating required of the base in the magnesium fluoride process. This heat treatment also places limitations on the use of magnesium fluoride films on mirrors having plastic bases.

b. Abrasion and Chemical Resistance. Comparative tests made on glass mirrors having aluminum reflecting surfaces with silicon monoxide films and similar mirrors with hardened magnesium fluoride films showed that:

(1) The abrasion resistance of one type of film is approximately equal to that of the other.

(2) Both types of mirrors withstand immersion in boiling distilled water for indefinite periods, but immersion in boiling salt water (5-percent solution) completely destroys the magnesium fluoride film within 5 minutes while the silicon monoxide film is undamaged after 1 hour.

The effect of heating in air to high temperatures, of cooling to very low temperatures, and of various acids -- treatments to which silicon monoxide protected mirrors are immune -- was not determined for magnesium fluoride protected mirrors.

c. Reflectivity. The total visual reflectivity of magnesium fluoride protected mirrors is approximately equal to that of silicon monoxide protected mirrors. However, the magnesium fluoride protected mirrors show more diffuse reflection and therefore light losses and less precise control of reflected radiation because of diffusion. The greater diffuse reflection of magnesium fluoride protected mirrors is caused by the crystalline structure of the condensed magnesium fluoride.

21. Chemical Reactions Producing Silicon Monoxide. In 1907 and 1908, Henry Noel Potter<sup>1</sup> patented several methods for producing

1. U. S. Pat Nos 875,286; 875,675; 875,676; and 866,636.



silicon monoxide. However, descriptions of processes for producing silicon monoxide did not reach the literature until the more recent investigations of Biltz<sup>1</sup> and Zintl<sup>2</sup>. The processes which produce silicon monoxide at relatively low temperatures are as follows:

- (1) Heating  $\text{SiO}_2$  in an atmosphere of hydrogen:  
 $\text{SiO}_2 + \text{H}_2 \rightarrow \text{SiO} + \text{H}_2\text{O}$
- (2) Heating the following in a vacuum on the order of  $1 \times 10^{-4}$  mm Hg:
  - (a)  $\text{SiO}_2 + \text{Si} \rightarrow 2\text{SiO}$
  - (b)  $\text{SiO}_2$  in graphite crucible:  
 $\text{SiO}_2 + \text{C} \rightarrow \text{SiO} + \text{CO}$
  - (c) Si in metal oxide crucible:  
 $\text{Si} + \text{MeO} \rightarrow \text{SiO} + \text{Me}$
  - (d) Bonded silicates with Si:  
 $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{Si} \rightarrow \text{Al}_2\text{O}_3 + 4\text{SiO}$

Several experimenters have made evaporations by placing silicon dioxide in graphite crucibles or silicon in metal oxide crucibles and have assumed that the product was silicon dioxide. This assumption was not correct, as shown by electron diffraction patterns of amorphous silicon monoxide obtained with the products of equations (2)(b) and (2)(c).

For producing quantities of silicon monoxide in the laboratory, reaction (2)(a) is suitable. Quantities of very finely divided silicon and silicon dioxide are intimately mixed approximately in proportion to their molecular weights. This mixture is placed in the closed end of a silica combustion tube. The tube is then evacuated to approximately  $10^{-4}$  mm Hg, and inserted horizontally in a muffle furnace. Beginning at approximately 1100 C, silicon monoxide evolves from the heated mixture and condenses on the cooler parts of the tube surfaces. The fused silica tube can be used but once, for it recrystallizes after being heated to 1200 C.

The mixture of silicon dioxide and silicon can be used directly in the evaporation chamber, by heating in the evaporation boat, to produce protective films of silicon monoxide.

22. Domestic Manufacturers of Silicon Monoxide. When experiments were first made in this country on silicon monoxide protective films, no American firms could supply it, and the only available material was a sample brought from Germany. As the result of the work described in this report and the interest created by a paper thereon, read before a meeting of the Optical Society of America in October

1. Biltz and P. Ehrlich, *Naturwiss* 26, 188 (1938).

2. Zintl, *Z anorg allg Chem* 245, 1 (1940).

1946, two American firms have placed silicon monoxide on the market. These firms are the Union Carbide and Carbon Company, 30 East 42 Street, New York 17, New York; and The National Research Corporation, Boston 15, Massachusetts.

#### IV. CONCLUSIONS

23. Conclusions. It is concluded that:

- a. Front-surface mirrors are necessary whenever maximum reflectivity and/or highly accurate and precise control of optical reflections is required.
- b. Silicon monoxide protected front-surface mirrors have qualities which make them particularly suitable for use in military equipment under all climatic conditions.
- c. Silicon monoxide protected front-surface mirrors with aluminum reflecting surfaces on glass bases have reflectivities in the visible and infrared not significantly lower than those of the unprotected metal, absorb in the ultraviolet, are highly abrasion resistant, and are unaffected by temperatures up to 400 C and down to -70 C, by temperature shocks from -70 C to 100 C, by ice formation, by boiling in a 5-percent salt solution, and by most acids.
- d. Silicon monoxide protected front-surface mirrors are much superior in corrosion resistance to magnesium fluoride protected front-surface mirrors.
- e. Evaporated aluminum films are more suitable for the reflecting surfaces of front-surface mirrors than silver films.

#### V. RECOMMENDATION

24. Recommendation. It is recommended that silicon monoxide protected front-surface mirrors with aluminum reflecting surfaces be used in military equipment which requires maximum reflectivity and/or precise control of visible or infrared radiation by mirrors subject to exposure to natural conditions.

Submitted by:

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APPENDIX A

## AUTHORITY

<u>Item</u>	<u>Page</u>
Letter from the Chief of Engineers to the Engineer Board, Dated 14 October 1946, File 400.1 (XR 750), Subject: Infrared Optical Materials, Approval of Military Charac- teristics and Authorization of Development Project XR 750, with one inclosure	23

WAR DEPARTMENT  
Office of the Chief of Engineers  
Washington

ENGNC (14 Oct 46)

14 October 1946

SUBJECT: Infrared Optical Materials, Approval of Military Characteristics and Authorization of Development Project  
XR 750

TO: The President  
The Engineer Board  
Fort Belvoir, Virginia

1. Reference is made to inclosed copy of Corps of Engineers Technical Committee Item 1039, dated 16 September 1946, subject: "Infrared Optical Materials, Approval of Military Characteristics and Authorization of Development Project XR 750," with attached approval sheet wherein the Military Characteristics, Plan of Development were approved and Project XR 750 assigned to the Corps of Engineers.

2. It is requested that the Engineer Board initiate development under this project in accordance with the Military Characteristics and Plan of Development as approved by Research and Development Division, War Department General Staff.

BY ORDER OF THE CHIEF OF ENGINEERS:

/s/ J. A. Ostrand, Jr.  
J. A. OSTRAND, JR.  
Colonel, CE  
Chief, Research and  
Development Division

1 Incl:  
Mimeo cy of Item 1039  
CETC Meeting #160 dtd  
16 Sept 1946

APPROVAL FOR 750

WAR DEPARTMENT  
OFFICE OF THE CHIEF OF ENGINEERS  
WASHINGTON 25, D. C.

Item 1039  
CETC Meeting #160

ENGINE

16 September 1946

SUBJECT: INFRARED OPTICAL MATERIALS, Approval of Military Characteristics and Authorization of Development Project  
XR 750

TO: Corps of Engineers' Technical Committee

FROM: Subcommittee on Development

1. REFERENCE:

Letter from Engineer Board to Chief of Engineers, file No. 400.1 (XR 750), subject: "Request for Project Infrared Optical Materials," dated 1 August 1946, with two inclosures thereto.

2. PURPOSE:

To develop optical materials which have special properties for the transmission, refraction, and reflection of infrared radiation for use as filters for infrared light sources and for protective coverings and optical elements of infrared equipment and to develop techniques for laboratory and production line testing of the optical and physical properties of such materials.

3. DISCUSSION:

a. The materials covered by this project are described as follows:

- (1) Near Infrared filters, as used on the sniper-scope, airborne beacon, searchlights, and vehicle driving equipment: Under Projects XR 441, Infrared Equipment, and XRS 441, Service for Near Infrared Equipment, the Engineer Board has investigated or developed light source filters of dyed glass, lacquer coatings, and dyed plastic sheets. None of these materials has been entirely satisfactory for field use, due to incomplete filtering out of visible light or cracking and optical deterioration under high temperatures. Development of heat-resistant near infrared filter materials with a sharp cut-off of

visible light and a high transmission of infrared radiation will materially increase the usefulness and reliability of near infrared devices.

- (2) Band pass or interference filters, as proposed for use on thermal imaging devices: Under Project XRS 578, Service for Far Infrared Equipment, the Engineer Board has initiated research on the development of thermal imaging devices capable of enabling night vision by the utilization of the far infrared radiation from objects. Development of band pass or interference filters transmitting only those wavelengths which are dominant in the radiation from the target object and to which the detecting elements are most sensitive will provide better operation of the imaging device by reducing the response band and minimizing or eliminating scatter and background interferences. In addition, such filters will simplify the optical correction systems of such devices, and will be of value in laboratory test equipment.
- (3) Protective windows, as used on the Penrod and various heat sensitive elements, such as the thermistor bolometer: Under Projects XR 514, Far Infrared Detecting Equipment, and XRS 578, Service for Far Infrared Equipment, the Engineer Board has investigated several materials which are transparent to longer wavelength infrared radiation, and which can be used as windows to protect heat sensitive elements from the effects of moisture and the noise induced by air currents. The materials thus far investigated include sheets of pliofilm, polyethylene, and silver chloride, and crystals of rock salt and lithium fluoride. Each material developed to date has some weakness, either fragility, deterioration under moisture, or inferior transmission of radiation. The provision of moisture proof protective window materials which will have high infrared transmission and withstand normal field usage is an essential part of the development of far infrared detecting devices.
- (4) Refractive optical materials, necessary for the development of simpler, more efficient and rugged infrared optical devices: The Engineer

Board has initiated an intensive program to duplicate the thallium halide crystals used in German heat detecting equipment, and now has two German scientists at Fort Belvoir to supply the detailed techniques of manufacture. This program will be continued, and other synthetic crystals of less critical material than thallium will be investigated. The establishment of a reliable source of supply of such material is of prime importance in the development of new heat detecting equipment.

- (5) Protective and Reflective coatings, as used on the reflectors of the Penrod and light source of the sniperscope: Under Project XRS 578, Service for Far Infrared Equipment, the Engineer Board has initiated research on high vacuum techniques for producing protection coatings of silicon monoxide on reflectors. It is proposed to expand this program to include coatings with other materials to give surfaces of adequate hardness, high reflectivity and selective reflectance to infrared radiation. The efficiency of any type of heat detecting equipment containing reflecting surfaces can be materially improved by use of such coatings on front surface reflectors.
- (6) Low reflectance optical coatings, as used on the telescope lenses of the Sniperscope M-2: Various films have been applied to standard optical devices during the recent war, for the purpose of decreasing reflection and increasing transmission, thus materially increasing image contrast and resolution. It is proposed to study the techniques used in applying such materials, and extend their use to optical elements of infrared equipment.

b. There are at present no entirely satisfactory infrared optical materials, even though considerable research on this problem has been conducted by the NDRC and other research agencies. The lack of satisfactory materials, such as filters, protective windows, refractive and reflective materials, and low reflectance coatings, has limited the performance of present infrared equipment. It is believed that the initiation of the subject project will result in more satisfactory materials thereby resulting in better performance of the present and future infrared equipment. The agencies interested in the subject project are Signal Corps, Ordnance Department, Army Air Forces, and the Navy Department.



c. Reference is made to Plan of Development attached as Exhibit "B". All presently available materials as well as newly developed or improved infrared optical materials will be studied, catalogued, and evaluated. Basic research to be conducted at the Engineer Board will consist of the following: growth of synthetic crystals; application of low reflectance coatings to optical elements; applications of high reflectance coatings to mirrors and reflectors; preparation of interference filters and filter mirrors; preparation of inorganic heat-resistant filters. Studies will be conducted on the problems of photometric standards, quantity production, and manufacturing techniques of infrared optical materials. Contracts will be let with various laboratories for the development of improved infrared optical materials. New materials, as they are developed, will be incorporated in existing equipment for evaluation. Specifications for materials will be maintained current. Liaison will be maintained with interested agencies.

d. No special equipment of other services will be required.

e. It is estimated that the project as presently planned will require three years to complete at a total cost of \$200,000.

f. The subject project should be assigned a priority of 2-A inasmuch as it will result in new materials that possess such marked superiority over existing materials that complete replacement will be justified.

#### 4. RECOMMENDATIONS:

The Subcommittee recommends:

a. Adoption of Military Characteristics as shown in Exhibit "A".

b. Approval of Project XR 750 Infrared Optical Materials, and assignment to the Corps of Engineers.

c. Procurement of such equipment as may be required for engineering tests in connection with development.

d. Assignment of Priority 2-A to Project No. XR 750.

e. Security classification of "Restricted" be assigned to the project, Military Characteristics and Plan of Development.

#### EXHIBITS:

"A" - Military Characteristics for Infrared Optical Materials.

"B" - Plan of Development.

EXHIBIT "A"

MILITARY CHARACTERISTICS  
FOR  
INFRARED OPTICAL MATERIALS

1. Transmission of useful infrared radiation shall be the maximum obtainable.
2. Materials designed for use as filters shall have a minimum transmission of those wavelengths which are to be excluded.
3. The transmission properties and physical strength shall be unaffected by the temperatures resulting through use with associated equipment, in ambient temperatures from -70 F to 150 F, or by heat shocks from maximum equilibrium temperatures to 70 F.
4. Materials shall be moisture and fungus resistant, and shall be capable of withstanding normal field usage.
5. Materials shall have physical properties suitable for various treatments, as being blown, cast, machine ground, or polished.
6. Materials shall be adaptable to manufacture in quantity production with close control of optical and physical properties.

## EXHIBIT "B"

## PLAN OF DEVELOPMENT

Project No. XR 750

Infrared Optical Materials

1. The work under this project will be directed towards collection of all pertinent information and development of new or improved infrared optical materials to be considered as a stockpile from which may be selected the best available components for incorporation in new or modified items of infrared equipment as they are developed.

2. All presently available materials will be studied, catalogued, and samples will be obtained, through library research, contact with manufacturers and other research agencies, and evaluation of captured enemy equipment.

3. Research will be conducted at the Engineer Board Laboratories on important basic studies, of which the following list may be considered typical:

a. Growth of sizeable crystals of thallium halides and other synthetic crystals, and study of methods of shaping, grinding, and polishing of such crystals.

b. Application of low reflectance coatings to optical elements which are designed for transmission of infrared radiation, and comparative tests to determine the most suitable methods of applying these coatings.

c. Application of high reflectance materials, by evaporation to reflectors in order to provide surfaces of adequate hardness, high reflectivity and selective reflectance to infrared radiation.

d. Application of protective coatings, by evaporation to mirrors and reflectors in order to provide more durable surfaces and to prevent early tarnishing and surface deterioration.

e. Preparation of interference filters and filter mirrors for use in the infrared region of the spectrum, and study of methods of application.

f. Preparation of inorganic heat-resistant filters which will cut off radiation to which caesium-silver-oxide is sensitive, and transmit that to which lead sulfide is sensitive.

4. Studies will be conducted to establish definite photometric standards for the comparison and evaluation of infrared optical materials.

5. Contracts will be let with reliable and suitably equipped university or industrial laboratories for development of improved infrared optical materials.

6. Problems of quantity production will be studied and samples of the more important materials will be procured from capable firms to insure adequate facilities, should quantity production be required. Detailed description of manufacturing techniques will be prepared for each new item.

7. As fast as promising new materials become available, these will be incorporated into existing and subsequently developed infrared equipment for engineering and service tests. The results of these tests will be used to guide further development of the materials.

8. Specifications for newly developed materials will be kept current so that limited procurement can be accomplished if and when required.

9. Liaison with the Signal Corps, Ordnance Department, Army Air Forces, and the Navy Department will be maintained to afford the interchange of samples of new materials and technical data and to avoid unnecessary duplication of effort.

10. Interim reports will be submitted as the work progresses, including recommendations for use based on engineering and service tests. Upon completion of development and tests, a final report will be submitted.

~~RESTRICTED~~

TITLE: Silicon Monoxide Protected Front-Surface Mirrors - Project 8-23-02-002  
(XR-750)

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ORIG. AGENCY : Engine Research and Development Lab., Fort Belvoir, Va.

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ABSTRACT:

The structure and properties of evaporated thin films of Al and Ag were studied and a simple, high-vacuum evaporation process for producing high-reflecting front-surface mirrors with durable protective films of SiO<sub>2</sub> is described. Al is selected as the reflecting material because evaporated Al films not only adhere to the mirror base with greater tenacity but also have a high reflectivity in nearly all useful spectral ranges and a much finer grain and smoother surface than similar Ag films. For protective films, SiO<sub>2</sub> was selected after investigation of the oxides of silicon. SiO<sub>2</sub> is evaporated onto the mirror surface from electrically heated W, Ta, or Mo boats. The properties of MgF<sub>2</sub> protected mirrors are compared with those of SiO<sub>2</sub> protected mirrors. Results indicate that SiO<sub>2</sub> protected front-surface mirrors are superior in corrosion resistance.

DISTRIBUTION: Copies of this report obtainable from CADO.

(1)

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